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m-Tolunitrile–H_2O complex: Isomers and methyl torsional potentials analyzed by the time-dependent density-functional theory

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Abstract

Density-functional theory (DFT) and time-dependent DFT (TD-DFT) were employed to calculate methyl torsional potentials of the *m*-tolunitrile monomer and two isomers of *m*-tolunitrile–H_2O complex. Geometries in their ground electronic states (S_0) were optimized at fixed torsional angles of 10-degree intervals with DFT. Torsional potentials in their first excited singlet electronic states (S_1) were obtained by calculating vertical excitation energy with TD-DFT for each optimized geometry in S_0. By comparing torsional potentials obtained by the calculations with those determined by analyzing observed torsional frequencies, we could determine the geometries of two isomers of *m*-tolunitrile–H_2O complex that had been observed spectroscopically.

Keywords: Internal rotation; Torsional potential; *m*-Tolunitrile–H_2O complex; DFT calculations

1. Introduction

There have been many studies of the methyl torsional motions in aromatic molecules because the motions are considered to play important roles in the dynamics of the molecules and their complexes. We have been studying methyl torsional potentials of aromatic molecules forming complexes with a rare gas atom or a small molecule [1,2]; we believe that the detailed investigation of changes of torsional potentials upon the complex formation is profitable to elucidate the role of torsional motion in dynamics of molecular complexes.

We have previously reported the methyl torsional potential of *m*-tolunitrile–H_2O complex in the S_1 state [2]. The torsional potential was determined with the conventional analytical technique [3,4] from the observed torsional frequencies measured by the laser-induced fluorescence (LIF) and hole-burning spectroscopies. Two isomers of the 1:1 complex of *m*-tolunitrile with H_2O were found to coexist in the supersonic jet: one complex has a threefold torsional potential similar to the potential of the monomer, while the torsional potential for the other complex has the barrier of nearly sixfold symmetry lower than that for the monomer. The former and the latter isomers were tentatively assigned to the geometries in which H_2O stays beside the cyano group at the opposite and the same sides of the methyl group, respectively, since the methyl group nearer to H_2O seemed to be perturbed more. However, we did not have direct basis for the assignment. Analyses for determining potentials gave no information on the geometries of the complexes.

In the present study, we tried to make unequivocal assignments of the observed species to the isomers with the aid of quantum chemical calculations. Density-functional theory (DFT) and time-dependent density-functional theory (TD-DFT) calculations were employed for estimation of torsional potentials of *m*-tolunitrile and its H_2O complexes in the ground electronic (S_0) and the first electronically excited singlet (S_1) states, respectively. Firstly, we checked whether the calculation technique could reproduce the methyl torsional potentials for the *m*-tolunitrile monomer in S_0 and S_1 which had been well analyzed. Then the technique was

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applied to the H_2O complexes. By comparing potentials obtained by calculations and those obtained by analyzing observed torsional frequencies, we could make unequivocal assignments. In this paper, the calculation procedure together with the obtained results is described.

2. Computational detail

Optimization of geometries and calculation of energies were performed for the *m*-tolunitrile monomer and its H_2O complexes with Gaussian 98 [5]. Programs made in our laboratory were used for obtaining torsional frequencies from the torsional potentials determined with the quantum-chemical calculations. Details of the calculations were as follows.

Firstly, torsional potentials in S_0 were calculated with the DFT (B3LYP/6-31G**) method: optimized geometries and their energies were calculated with the torsional angles fixed at intervals of 10 degrees. Torsional potentials in S_0 were obtained by plotting calculated energies against the torsional angle. Then, vertical excitation energies were calculated with the TD-DFT (TD-B3LYP/6-31G**) method for the geometries optimized at different torsional angles in S_0. Torsional potentials in S_1 were obtained by plotting sums of the potential energy in S_0 and the excitation energy at each torsional angle.

Torsional potentials obtained by the DFT and TD-DFT calculations were expressed with the sum of six components, $V_{3n}(n = 1 - 6)$, as follows:

$$V(\phi) = \frac{1}{2}\sum_{n=1}^{6} V_{3n}[1 - \cos(3n\phi)]. \qquad (1)$$

Here, ϕ denotes the torsional angle, and V_{3n} corresponds to the $3n$-fold component of the torsional potential. Torsional frequencies were calculated by assuming the potential expressed by Eq. (1) and by applying the conventional technique [3,4]. The internal-rotational constants, B, in S_0 were calculated from the optimized geometries, and those in S_1 were varied as a parameter so that the calculated frequencies reproduce the observed ones well.

3. Results and discussion

The conventional notation is used for the levels of internal rotation of *m*-tolunitrile [6,7]. The vibronic states due to the methyl torsion are denoted by $0a_1$, 1e, 2e, $3a_1$, $3a_2$, 4e and so on, using a combination of the rotational quantum number in a one-dimensional free rotor and the symmetry species.

3.1. Calculations for monomer

Energies of the *m*-tolunitrile monomer calculated at different torsional angles by the B3LYP/6-31G** method are summarized in Table 1, where the energies of *m*-tolunitrile at the torsional angles of every 10 degrees relative to that at the torsional angle of 0 degree are shown. The torsional angle of 0 degree is defined as the conformation in which one of the three hydrogen atoms in the methyl group points to the cyano group on the plane of phenyl ring.

In Fig. 1a, methyl torsional potential of the *m*-tolunitrile monomer in S_0 obtained by the B3LYP/6-31G** calculations (shown with ◆) is compared with that obtained by the analysis of experimentally observed torsional frequencies (solid line) [1,7]. The calculations at smaller intervals of torsional angle revealed that there exist small rises and falls of less than 1 cm^{-1} in the potential at the torsional angles less than 20 degrees. It seems, however, insignificant to pursue the small variation of less than 1 cm^{-1}, which is much smaller than the zero-point energy of about 6 cm^{-1} for the torsional motion.

The potential obtained by the calculations was found to be different considerably from that obtained by the analysis of observed torsional frequencies. The bottom of the potential is flat in the former but double minimum in the latter, while the overall heights of both potentials are almost same. Since the potential obtained by the analysis of experimental data was determined only so as to reproduce the three observed frequencies by adjusting three potential parameters, V_3, V_6 and B, it does not necessarily reproduce the actual potential perfectly.

In Table 2, torsional frequencies of *m*-tolunitrile calculated for S_0 and S_1 from the potential data in Table 1 are compared with the observed ones. In the calculations for S_0, the internal-rotational constant of 5.41 cm^{-1} obtained from the optimized geometry was used. Calculated frequencies reproduced observed ones well, suggesting that the potential obtained by the B3LYP/6-31G** calculations can be another candidate of the torsional potential.

Table 1
Relative energies (in cm^{-1}) at different torsional angles obtained by the B3LYP/6-31G** and TD-B3LYP/6-31G** calculations

Torsional angle (degree)	Monomer		H_2O Complex (I)		H_2O Complex (II)		H_2O Complex (III)	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	0.3	−7.3	0.1	−4.7	0.2	−7.6	0.2	−3.0
20	0.6	−26.3	2.5	−14.3	1.5	−26.3	1.2	43.1
30	5.5	−41.1	7.2	−19.9	7.0	−41.8	5.0	115.0
40	11.2	−47.2	14.0	−16.4	15.1	−46.8	11.9	208.7
50	16.3	−46.0	19.8	−8.6	22.7	−43.2	18.1	291.1
60	19.1	−44.2	21.5	−5.4	25.4	−41.3	22.1	338.6